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**The production of nitric oxide in the stratosphere
by oxidations of nitrous oxide**

by M. NICOLET and W. PEETERMANS

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FOREWORD

"The Production of nitric oxide in the stratosphere by oxidations of nitrous oxide" follows "L'Oxyde azoteux dans la stratosphère" by M. Nicolet and E. Vergison, Aeronomica Acta A n° 90 and will be published in Annales de Géophysique.

AVANT-PROPOS

"The Production of nitric oxide in the stratosphere by oxidations of nitrous oxide" fait suite à "L'Oxyde azoteux dans la stratosphère" par M. Nicolet et E. Vergison, Aeronomica Acta A n° 90 et sera publié dans les Annales de Géophysique.

VOORWOORD

"The Production of nitric oxide in the stratosphere by oxidations of nitrous oxide" is het vervolg van "L'Oxyde azoteux dans la stratosphère" door M. Nicolet en E. Vergison, Aeronomica Acta A nr 90, en zal verschijnen in Annales de Géophysique.

VORWORT

"The Production of nitric oxide in the stratosphere by oxidations of nitrous oxide" ist eine Folge zu "L'Oxyde azoteux dans la stratosphère" durch M. Nicolet und E. Vergison, Aeronomica Acta A 90 und wird in Annales de Géophysique herausgegeben werden.

THE PRODUCTION OF NITRIC OXIDE IN THE STRATOSPHERE BY OXIDATIONS OF NITROUS OXIDE

by

M. NICOLET and W. PEETERMANS

Abstract

The reaction of the electronically excited oxygen atom $O(^1D)$ with nitrous oxide, suggested by Nicolet as a natural source of nitric oxide in the stratosphere, may lead to a production of the order of $(1 \pm 0.5) \times 10^8$ NO molecules $\text{cm}^{-2} \text{sec}^{-1}$.

The predictability of a reliable estimate of the NO production in the stratosphere depends strongly on the exact determination of the variable flux from the troposphere of N_2O molecules; of the order of $(1 \pm 0.5) \times 10^9$ molecules $\text{cm}^{-2} \text{sec}^{-1}$.

In situ sources of stratospheric N_2O seem to be negligible and the introduction of nitrogen oxides by upward transport from the troposphere and of nitric oxide by downward transport from the mesosphere requires adequate conditions at the tropopause and strato-pause; respectively.

An assumed operation of 500 SST aircraft in the stratosphere would lead to an artificial emission of nitric oxide molecules of the same order of magnitude as the natural production from nitrous oxide.

Résumé

La réaction du protoxyde d'azote avec l'oxygène atomique dans son premier état excité $O(^1D)$, suggérée par Nicolet comme une source naturelle d'oxyde d'azote dans la stratosphère, conduit à une production de l'ordre de $(1,0 \pm 0,5) \times 10^8$ molécules $NO \text{ cm}^{-2} \text{ sec}^{-1}$.

Une détermination précise de la production stratosphérique de NO dépend de l'exacte nature du flux de molécules N_2O de la troposphère à la stratosphère qui peut être variable suivant les conditions atmosphériques au voisinage de la tropopause. Ce flux est de l'ordre de $(1 \pm 0,5) \times 10^9$ molécules $N_2O \text{ cm}^{-2} \text{ sec}^{-1}$.

Il apparaît que les sources possibles de N_2O dans la stratosphère ne présentent pas beaucoup d'importance. D'autre part, l'introduction d'oxydes d'azote par transport vertical à partir de la troposphère ou de la stratosphère requiert des conditions spéciales dans l'un ou l'autre cas.

Enfin, une flotte aérienne, qui serait de 500 avions supersoniques volant dans la stratosphère, conduirait à un apport artificiel d'oxydes d'azote du même ordre de grandeur que la production naturelle résultant de l'oxydation du protoxyde d'azote.

Samenvatting

De reactie van N_2O met atomaire zuurstof in de eerste geëxciteerde toestand $O(^1D)$, voorgesteld door Nicolet als een natuurlijke bron van stikstofoxyde in de stratosfeer, kan ongeveer $(1 \pm 0,5) \times 10^8$ NO molekulen $cm^{-2} sec^{-1}$ voortbrengen.

Een juiste bepaling van de NO-productie in de stratosfeer is afhankelijk van de nauwkeurige kennis van de flux der N_2O molekulen van de troposfeer naar de stratosfeer. Deze flux die veranderlijk is al naargelang de atmosferische gesteldheid in de buurt van de tropopauze, is van de orde $(1 \pm 0,5) \times 10^9$ molekulen $N_2O cm^{-2} sec^{-1}$.

Mogelijke bronnen van N_2O in de stratosfeer hebben slechts weinig belang. Anderzijds, zijn speciale voorwaarden, vereist voor het invoeren van stikstofoxydes door vertikaal transport vanaf de troposfeer of de stratosfeer.

Een vloot van 500 supersonische vliegtuigen welke in de stratosfeer zouden vliegen zou tot een kunstmatige bijdrage van stikstofoxyden leiden die van dezelfde grootte-orde zou zijn als de natuurlijke productie.

Zusammenfassung

Die Reaktion des N_2O mit die Sauerstoffatome im angeregten Zustand $\text{O}(^1\text{D})$, die durch Nicolet als die Hauptquelle des NO in der Stratosphäre erkannt wurde, produziert $(1 \pm 0,5) \times 10^8 \text{ NO Molekülen cm}^{-2} \text{ sec}^{-1}$.

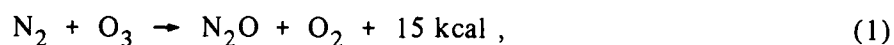
Eine genaue Berechnung des stratosphärischen NO hängt von dem Wert des N_2O Fluss aus der Troposphäre ab. Dieser N_2O Fluss ist zirca $(1 \pm 0,5) \times 10^9 \text{ cm}^{-2} \text{ sec}^{-1}$, aber ist sehr abhängig von der atmosphärischen Bedingungen in der Tropopause Höhe.

Die Produktion des N_2O in der Stratosphäre ist nicht sehr wichtig.

Zuletzt, 500 Überschallflugzeugflüge in der Stratosphäre bilden eine artifizielle Quelle für Stickstoffoxyden die mit die natürliche Produktion vergleichbar ist.

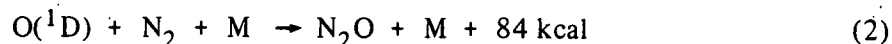
The formation of nitrous oxide, which is present in the troposphere with a mixing ratio of the order of 2.5×10^{-7} (Birkeland and Shaw, 1959; Rank *et al.*, 1962; Bowman and Shaw, 1963) has been discussed recently by Bates and Hays (1967) and measured extensively by a gas chromatographic method in the troposphere by Schütz *et al.* (1970) and Junge and Hahn (1971).

Further measurements have also been made by the same technique in the humid tropics by Lattue *et al.* (1970) and by a spectrographic technique in Massachusetts by Goody (1969). A few measurements have been made in the upper troposphere and lower stratosphere by Goody (1954), Seely and Houghton (1961), Goldman *et al.* (1970) and by Schütz *et al.* (1970). The microbiological source of the soil, suggested by Adel (1946, 1951), following his first observations (Adel, 1939, 1941) appears to be the origin of the N_2O molecules which are practically in uniform mixing in the troposphere (Goldberg and Müller, 1953). However, a chemical reaction such as

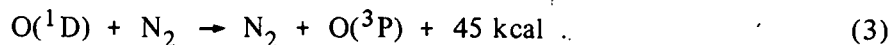


considered by Bates and Witherspoon (1952) in the first aeronomic study of N_2O , should be accepted as a production process if a reaction rate coefficient of not less than 10^{-28} cm^3 , which may be possible at 300°K according to Goody and Walshaw (1953), is appropriate. However, it appears, that such a reaction may require an activation energy of not less than 20 kcal.

Another reaction, which was also introduced by Bates and Witherspoon (1952),

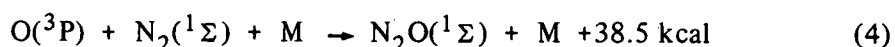


has not been considered to be a significant source by Bates and Hays (1967) since laboratory data show that reaction (2) is negligible compared with the quenching reaction



In fact, when the detailed processes are considered (Simonaitis *et al.*, 1972) it is clear that the chemical reaction between $O(^1D)$ atoms and N_2 molecules cannot play an aeronomic role in the generation of stratospheric N_2O . The efficiency of reaction (2) relative to reaction (3), which is of the order of 2.5×10^{-6} at 1000 torr total pressure, is about 100 times too small to produce a stratospheric effect in comparison with the transport of N_2O from the troposphere. A rate coefficient of $5 \times 10^{-34} \text{ cm}^6 \text{ sec}^{-1}$ for this process would be required to increase the actual N_2O concentration in the stratosphere.

Other chemical reactions which have been suggested for the formation of N_2O must be rejected as aeronomic reactions. The formation of atmospheric N_2O with $O(^3P)$ *normal* atoms is practically impossible ;



corresponds to two atoms approaching on a repulsive curve (cf. Stearn and Eyring, 1935; Reuben and Linnett, 1959; Clyne and Thrush, 1962) with a potential barrier of the order of 20 kcal before crossing the normal state $N_2(^1\Sigma)$ which dissociates into $N_2(^1\Sigma) + O(^1D)$. The rate coefficient is certainly less than $5 \times 10^{-38} \text{ cm}^6 \text{ sec}^{-1}$ (Stuhl and Niki, 1971). Similarly there is no possible relevant contribution by a radiative recombination such as

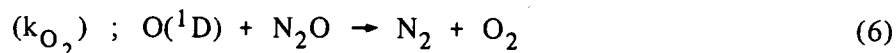


which was used with a rate coefficient of the order of $10^{-24} \text{ cm}^3 \text{ sec}^{-1}$ by Hesstvedt and Jansson (1969) and by Shimazaki and Laird (1970) in their determination of nitrogen oxides in the mesosphere. The introduction of such a reaction leads to unacceptable aeronomic concentrations.

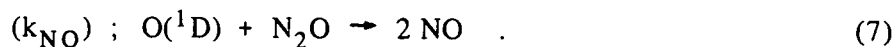
Thus, it seems that there is no important process which is involved in the N_2O production in the stratosphere; N_2O must come from the troposphere.

A reaction between N_2O and normal oxygen atoms $O(^3P)$ requires a very high activation energy of at least 25 kcal. (Fishburne and Edse, 1966) and is always negligible in the study of aeronomic problems. But the reaction of N_2O with excited oxygen atoms is well

established (Zelikoff and Aschelbrand, 1954; Castellion and Noyes, 1957). The $O(^1D)$ singlet oxygen atoms react with N_2O in two ways



and



According to Greenberg and Heicklen (1970), Goldman *et al.* (1971), Scott *et al.* (1971) and Simonaitis *et al.* (1971) the ratio k_{NO}/k_{O_2} is not very different from unity even when the translational energy of the excited oxygen atoms is high.

With a value of the order of $2 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$ (Young *et al.*, 1968) for the rate coefficient of the $O(^1D) + N_2O$ reaction, the following working values can be adopted for the rate coefficient of reactions (6) and (7) (Scott *et al.*, 1971; Simonaitis *et al.*, 1972)

$$k_{O_2} = 1 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1} \quad (8)$$

and

$$k_{NO} = 1 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1} \quad (9)$$

Thus, as was shown by Nicolet (1970, 1971), reaction (7) is an important process for the formation of nitric oxide in the stratosphere. It may lead to a production of NO of $(1 \pm 0.5) \times 10^8 \text{ molecules cm}^{-2} \text{ sec}^{-1}$ according to Nicolet and Vergison (1971) or to $2 \times 10^7 \text{ cm}^{-2} \text{ sec}^{-1}$ according to McElroy and McConnell (1971).

Finally, in order to take into account all aeronomic processes, it is also necessary to consider the photodissociation of nitrous oxide molecules in the solar radiation field. In the earth's atmosphere, various spectral regions must be considered when the N_2O absorption cross sections are compared with the ozone and oxygen absorptions. The absorption cross sections of N_2O are well known (Zelikoff *et al.*, 1953, in the region of the O_2 Schumann-Runge continuum and bands. In the region of ozone absorption (Hartley and Huggins bands), where a very weak absorption was detected by Sponer and Bonner (1940), there are

measurements made by Thompson *et al.* (1963) to 2400\AA and by Young (cf. Bates and Hays, 1967) to the spectral limit near 3150\AA . The average cross sections which have been adopted, for spectral ranges of 500 cm^{-1} , are presented in Figs. 1 and 2; they vary from less than 10^{-23} cm^2 for $\lambda > 2500\text{\AA}$ to about 10^{-20} cm^2 near 2000\AA and up to 10^{-17} cm^2 in the Schumann-Runge continuum. Considering the number of photons available at the top of the earth's atmosphere (cf. Ackerman, 1971) the N_2O photodissociation coefficient at zero optical depth is

$$J_{\infty}(\text{N}_2\text{O}) = 4 \times 10^{-6}\text{ sec}^{-1} . \quad (10)$$

At the stratopause level (50 km) the photodissociation is due to radiation of (see Fig. 3) $1750\text{\AA} < \lambda < 2500\text{\AA}$, and

$$J_{50\text{ km}}(\text{N}_2\text{O}) (7 \pm 1) \times 10^{-7}\text{ sec}^{-1} . \quad (11)$$

In the stratosphere, above 20 km, the absorption by molecular oxygen and ozone leads to a rapid decrease of the photodissociation coefficient (Fig. 3). In the troposphere and lower stratosphere below 20 km, the photodissociation is due to the radiation which can reach the earth's surface at $\lambda < 3150\text{\AA}$. Therefore, the photodissociation coefficient depends strongly on the solar zenith angle (Fig. 4); it varies by a factor of about 50 in the lower stratosphere from $\sec \chi = 1$ to $\sec \chi = 4$, i.e. for an overhead sun and a solar zenith angle of about 70° , respectively. Such $J_{\text{N}_2\text{O}}$ values, which correspond to a specific ozone distribution with height (Nicolet, 1970) may vary since there are important variations in the vertical distribution of the ozone concentration below the peak in the lower stratosphere and upper troposphere. It is, therefore, possible that the photodissociation coefficients adopted below 20 km may change by a factor of 2; depending on special ozone distributions. The average rate illustrated in Fig. 4 corresponds to the values deduced by Bates and Hays (1967) since the absorption cross sections used for $\lambda > 2500\text{\AA}$ are identical. A very careful analysis is still required in order to determine the precise photodissociation coefficient due to solar radiation of $\lambda > 2500\text{\AA}$ since it determines the destruction of N_2O in the troposphere and lower stratosphere.

Another important aspect of the N_2O photodissociation is the nature of the dissociation products (Sponer and Bonner, 1940; Zelikoff *et al.*, 1953). Nicolet and Vergison

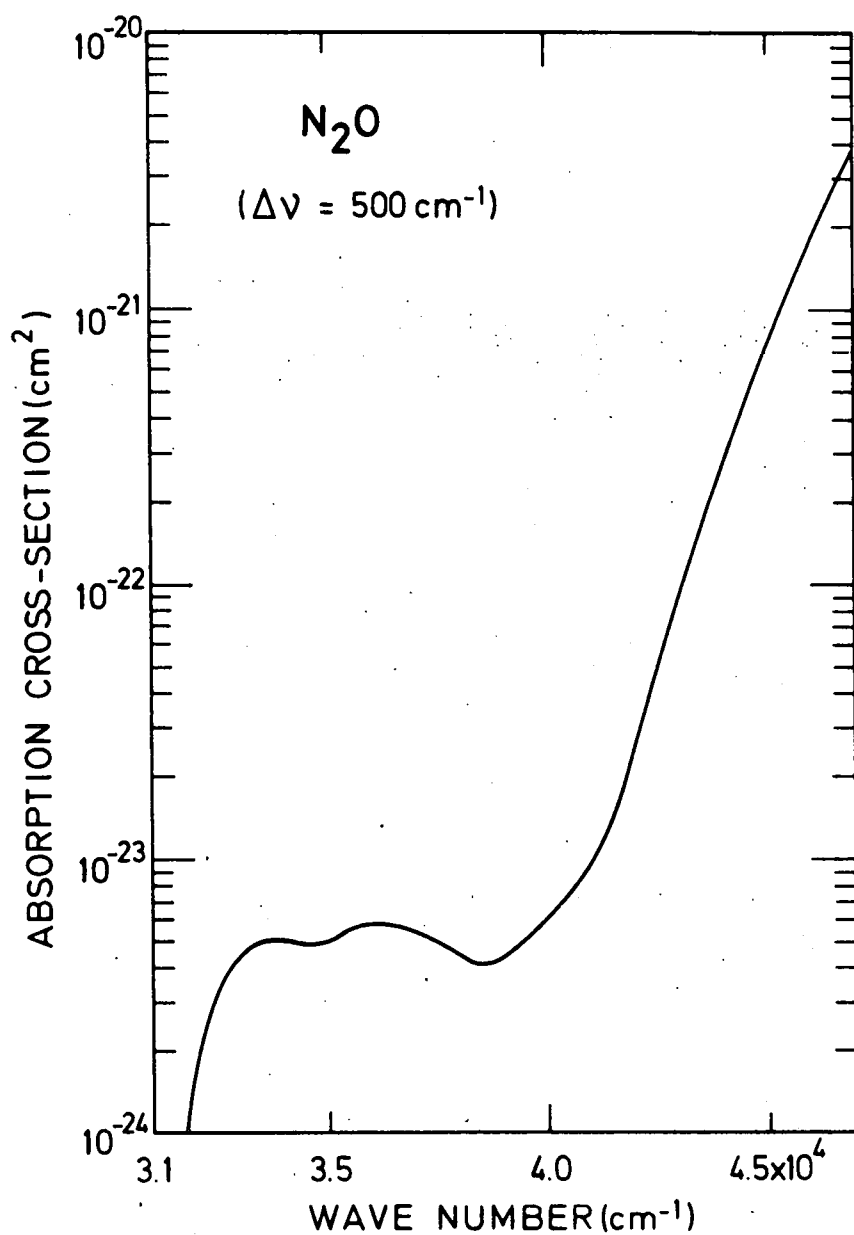


Fig. 1.- Average absorption cross section of N_2O adopted for $\Delta \nu = 500 \text{ cm}^{-1}$ between 3×10^4 and $4.5 \times 10^4 \text{ cm}^{-1}$. Absorption cross section identical to photodissociation cross section. See Bates and Hays (1967).

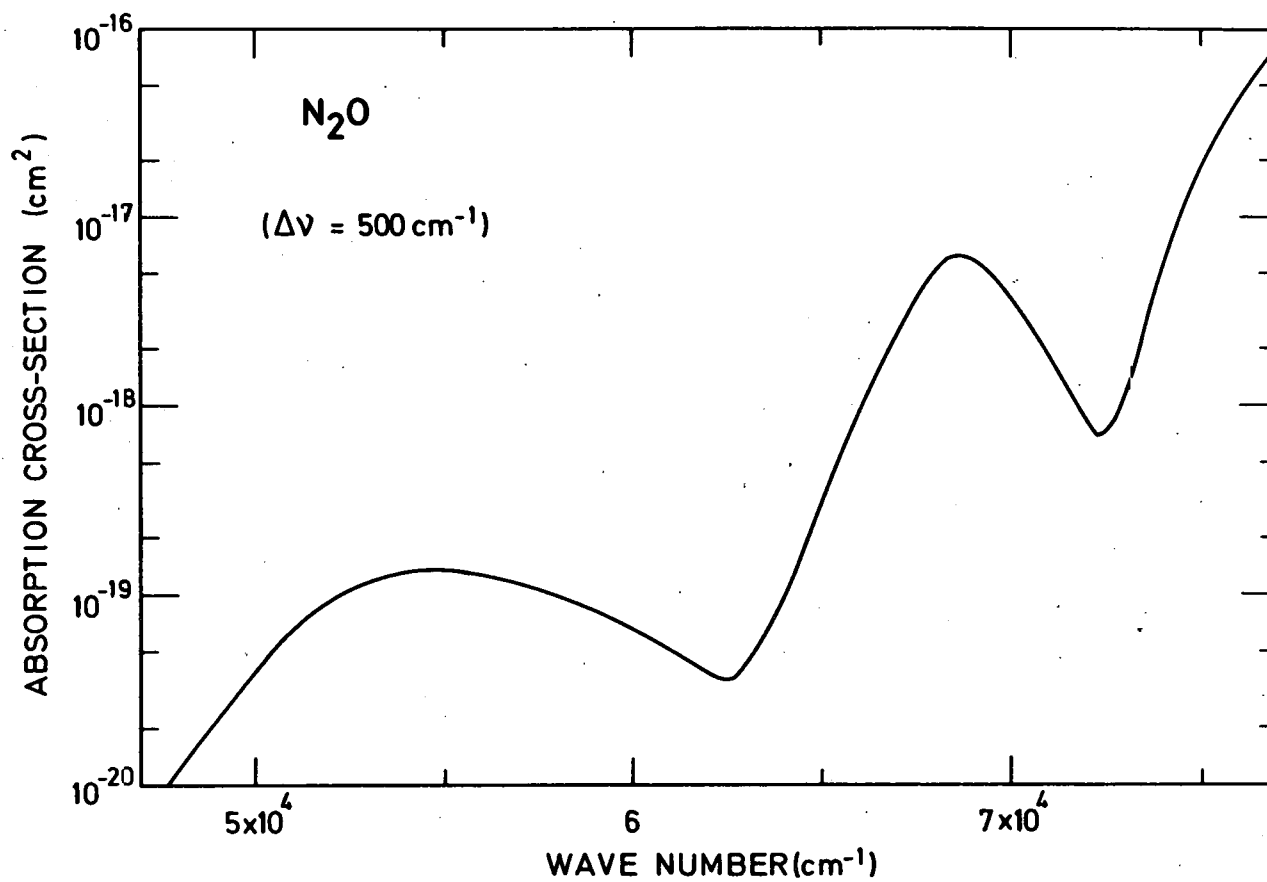


Fig. 2.- Average absorption cross section of N_2O adopted for $\Delta\nu = 500 \text{ cm}^{-1}$ between 4.5×10^4 and $7.5 \times 10^4 \text{ cm}^{-1}$. Absorption cross section identical to photodissociation cross section.

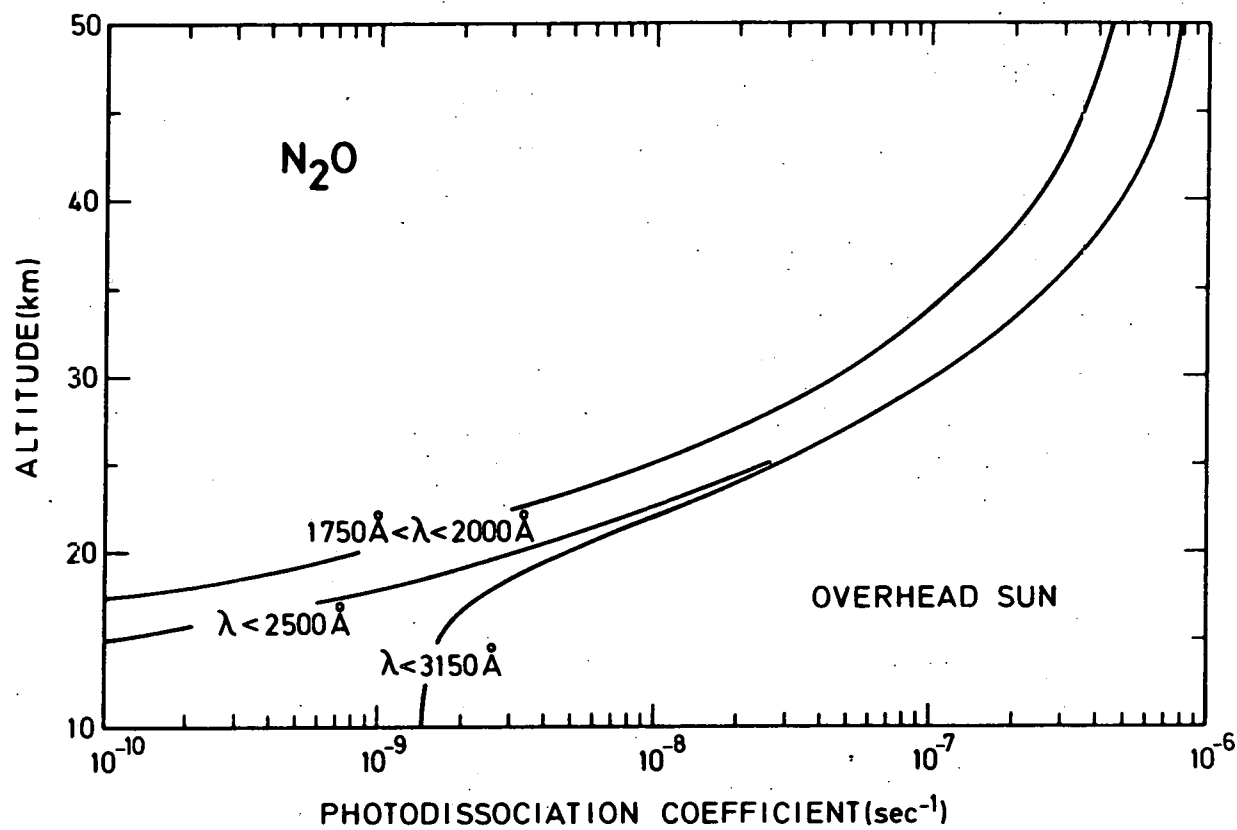


Fig. 3.- Photodissociation coefficient of N_2O for an overhead sun. In the troposphere and lower stratosphere, the effect is due to radiation of $\lambda > 2500 \text{ \AA}$; in the stratosphere the radiation which is involved corresponds to $1750 < \lambda < 2500 \text{ \AA}$.

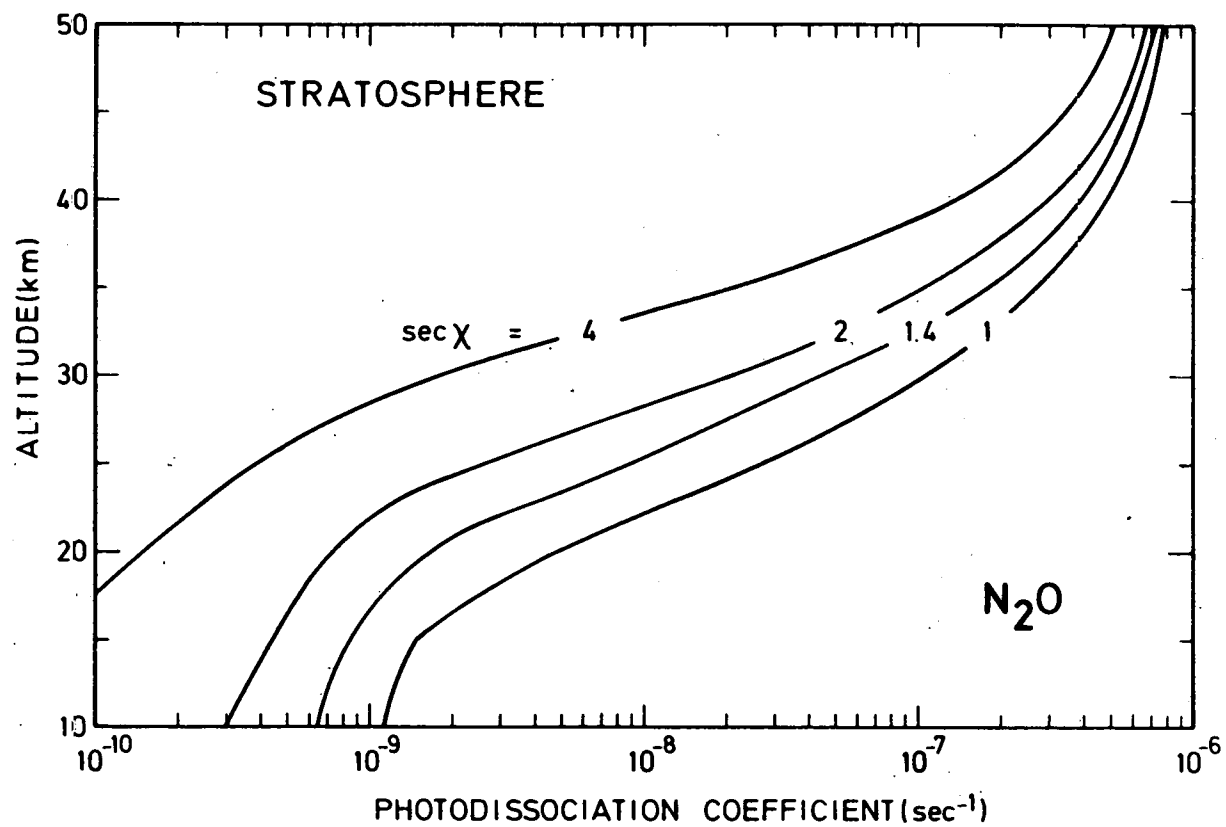
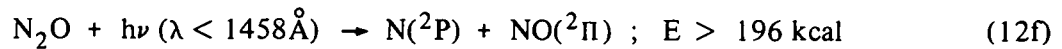
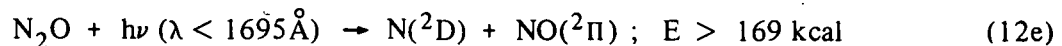
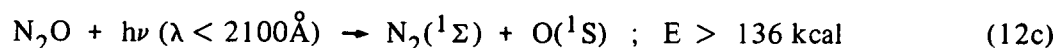
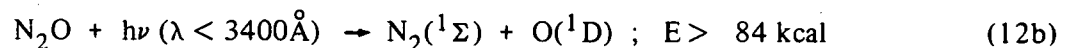
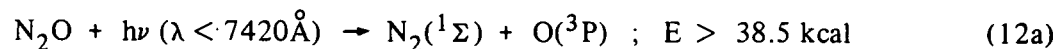


Fig. 4.- Photodissociation coefficient of N_2O in the stratosphere for various zenith angles :
 $\sec \chi = 1, 1.4, 2$ and 4 .

(1971) have shown that the principal *aeronomic* process involved in the stratosphere is the dissociation of N_2O into N_2 and O.

With a dissociation energy ($N_2O \rightarrow N_2 + O$) of 38.5 ± 0.2 kcal (Dibeler, 1967; Okabe, 1967) the thresholds for the various dissociation processes are as follows: (see Fig. 5)



The photodissociations (12a) and (12d) are considered to be negligible compared with (12b) and (12c) and with (12e) and (12f), respectively; the N_2O dissociation (12a) and (12b) does not occur with conservation of spin. Other processes, such as those involving excited states of N_2 and NO, have also been observed in the laboratory but since their thresholds are in the region of the Schumann-Runge continuum, they do not contribute to the aeronomic dissociation of N_2O in the stratosphere. For the same reason, processes (12e) and (12f) cannot play a role in the mesosphere and stratosphere. For $\lambda < 2500\text{\AA}$ two processes can be involved as far as the required threshold is concerned, namely processes (12c) and (12d). But if we consider the absorption analysis made by Holliday and Reuben (1968), the absorption between 1900\AA and 2500\AA must lead to $N_2 + O$ and not to $N + NO$ which is spin forbidden. Furthermore, recent experiments also show that the photodissociation of N_2O into N_2 and $O(^1D)$ must be the exclusive primary process. According to Preston and Barr (1971), at $\lambda = 2139\text{\AA}$ the formation of nitrogen atoms does not occur ($< 1\%$) and according to Simonaitis *et al.* (1972), the quantum yield of $O(^3P)$ at 2139\AA and 1849\AA for all possible sources is 0.02 ± 0.02 .

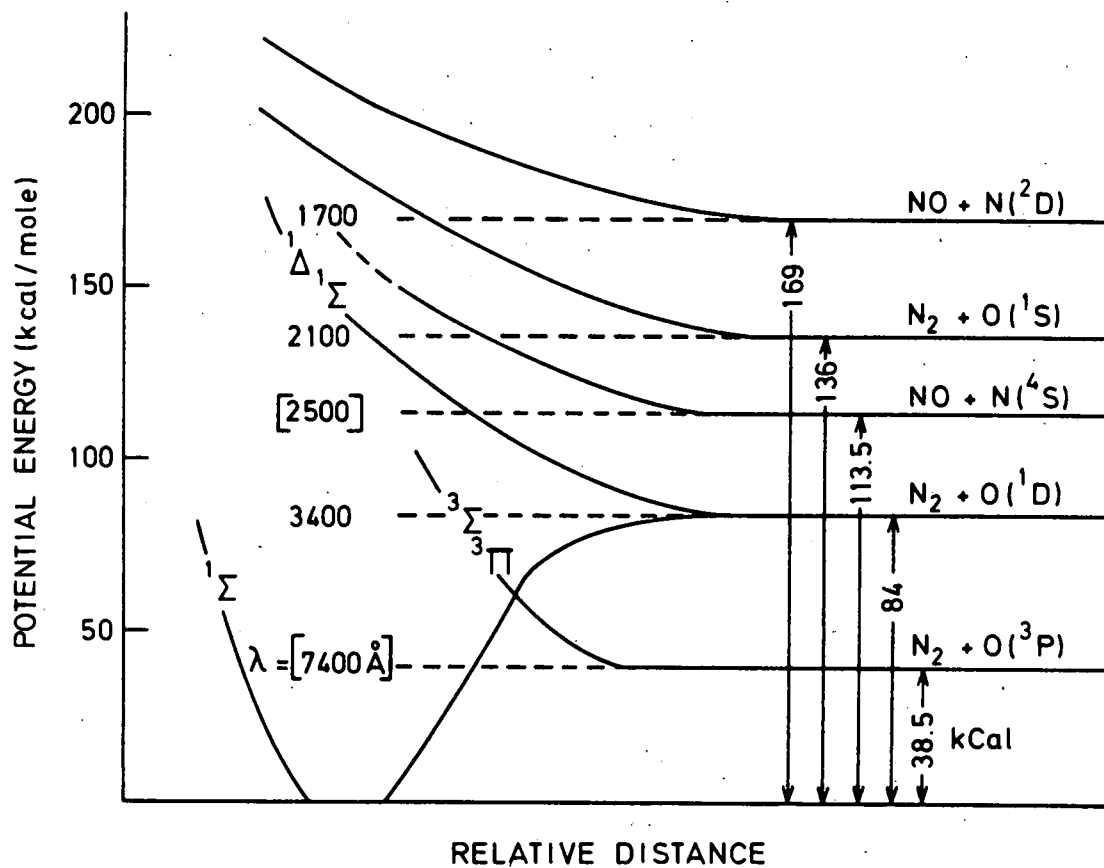


Fig. 5.- Dissociation curves for N₂O. For $\lambda > 1750\text{\AA}$ $\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}$.

Thus, it is clear that, in the stratosphere where the photodissociation results from radiation of wavelengths greater than 1900\AA , the exclusive primary dissociation process involving N_2O is the production of oxygen atoms and not of nitric oxide molecules. It appears, therefore, that nitric oxide cannot be produced in the stratosphere in the way suggested by Bates and Hays (1967) and adopted by Crutzen (1970) for a determination of the vertical distribution of nitrogen oxides in the stratosphere.

Nevertheless, as discussed later there is a formation of nitric oxide by process (18) in which $\text{O}(^1\text{D})$ atoms are formed by the photodissociation of atmospheric ozone. The photo-equilibrium abundance of $\text{O}(^1\text{D})$ atoms is determined by the balance of its production term, corresponding to ozone dissociation, with the loss term, corresponding to quenching by molecular oxygen and nitrogen; it is written

$$n[\text{O}(^1\text{D})] = \frac{n(\text{O}_3) J_3^*}{k_q [n(\text{N}_2) + n(\text{O}_2)]} \quad (13)$$

where J_3^* is the photodissociation coefficient leading to $\text{O}(^1\text{D})$ atoms and k_q is an average quenching rate coefficient for N_2 and O_2 .

If $k_q(\text{N}_2, \text{O}_2) = 5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$, which seems to be a good average value according to direct and relative laboratory measurements (Young *et al.*, 1968; Snelling and Bair, 1968; DeMore, 1969, 1970; Paraskevopoulos and Cvetanovic, 1969, 1971; Yamazaki, 1970; Noxon, 1970; Donovan *et al.*, 1970; Scott and Cvetanovic, 1971; Paraskevopoulos *et al.*, 1971; Gauthier and Snelling, 1971; Lowenstein, 1971; Gilpin *et al.*, 1971; Lissi and Heicklen, 1972), it should be noted that it corresponds to about 1/4 of the value of a average kinetic rate coefficient of the order of $2 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$.

If we consider the simple formula (McDaniel, 1964)

$$\frac{dE_1}{dt} = - 2 \frac{m_1 m_2}{(m_1 + m_2)^2} (E_1 - E_2) \nu_{12} \quad , \quad (14a)$$

we may determine the average rate at which kinetic energy is transferred from particles of type 1 (excited oxygen atoms) to particles of type 2 (atmospheric molecular oxygen and nitrogen); here, m refers to the particles mass, $m_1 = m(\text{O})$ and $m_2 = m(\text{N}_2, \text{O}_2)$; E is the

kinetic energy, and ν_{12} is the collision frequency of excited oxygen atoms with atmospheric molecules. Thus,

$$\frac{dE}{dt} = -\frac{1}{2} (E_1 - E_2) \nu_{12} \quad (14b)$$

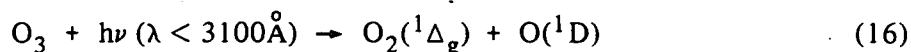
with

$$\nu_{12} = 10^{-11} T^{1/2} \left[1 + 1.75 \frac{E_1}{E_2} \right]^{1/2} \quad (15)$$

Expressions (14) show that the quenching of $O(^1D)$ by N_2 and O_2 will occur after a certain reduction of the translational energy of the excited atoms which are produced by photolysis of ozone with various excesses of kinetic energy. Fig. 6a illustrates the distribution of the total kinetic energy of O_2^* and O^* at various altitudes over equal energy ranges of 500 cm^{-1} . It is clear that the photodissociation of O_3 leads to kinetically hot $O(^1D)$ atoms if it is assumed that the excess energy is inversely proportional to the mass of a fragment. For example, a simple way is to assume here that 2/3 and 1/3 of the total kinetic energy available are for O atoms and O_2 molecules, respectively.

Furthermore, there are important differences between the lower and higher stratosphere due to the height variation of the ozone absorption. It can be seen (Fig 6b) that in the major part of the lower stratosphere the total translational energy (O_2 and O) is less than 5 kcal/mole, and, therefore, a quenching rate coefficient of $O(^1D)$ by N_2 and O_2 is perhaps not too far from $5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$, even if the quenching is related to the kinetic energy of the excited atoms. In any case, the experimental values of the reaction or quenching rates of excited atoms must be carefully checked before being used with sufficient accuracy for aeronomic purposes since a precision of a factor of two is not adequate.

An exact determination of the production of $O(^1D)$ atoms by the photolysis of the stratospheric ozone is also required. If, as it appears, the efficiency of $O(^1D)$ and $O_2(^1\Delta_g)$ production is not far from unity (DeMore and Raper, 1966) for the process



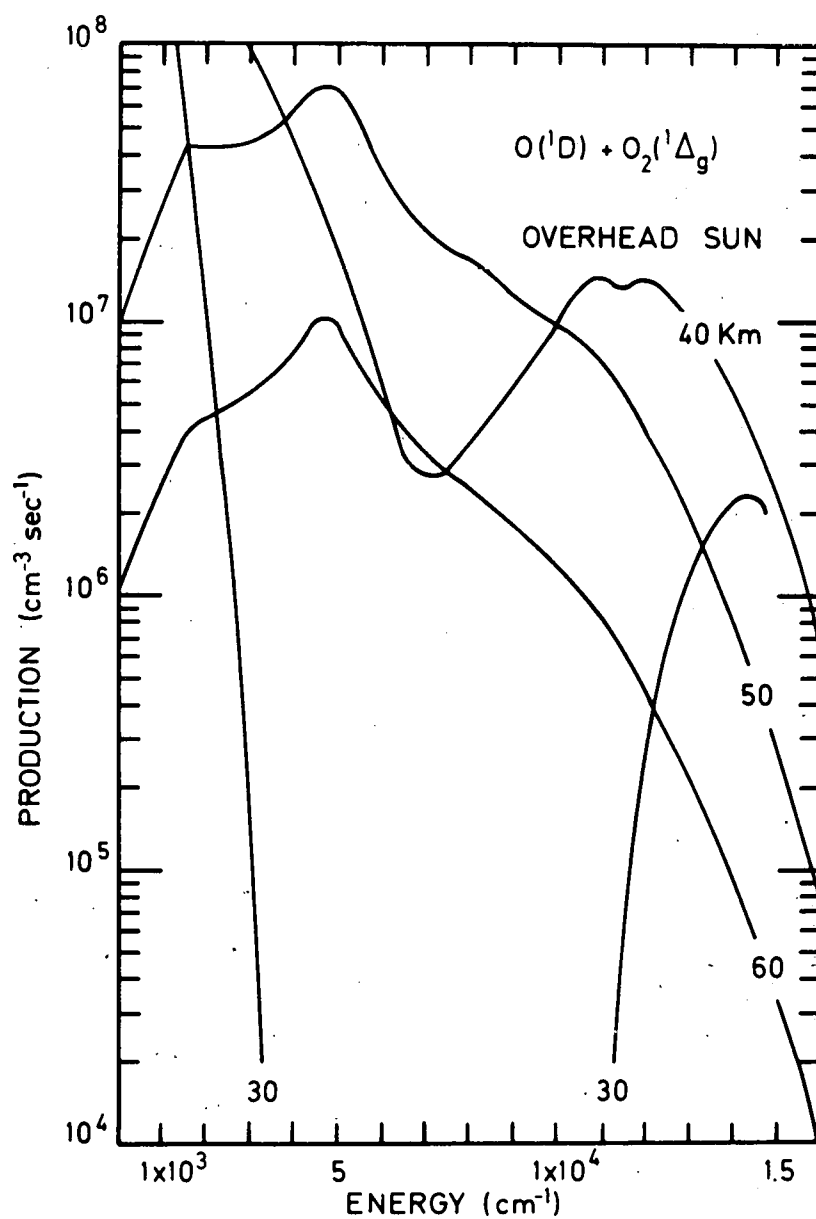


Fig. 6a.- Number of the fragments of the photodissociation process $\text{O}_3 + h\nu (\lambda < 3100\text{\AA}) \rightarrow \text{O}_2(^1\Delta_g) + \text{O}(^1\text{D})$ which are produced per cm^3 and sec over a spectral range of 500 cm^{-1} at various height levels.

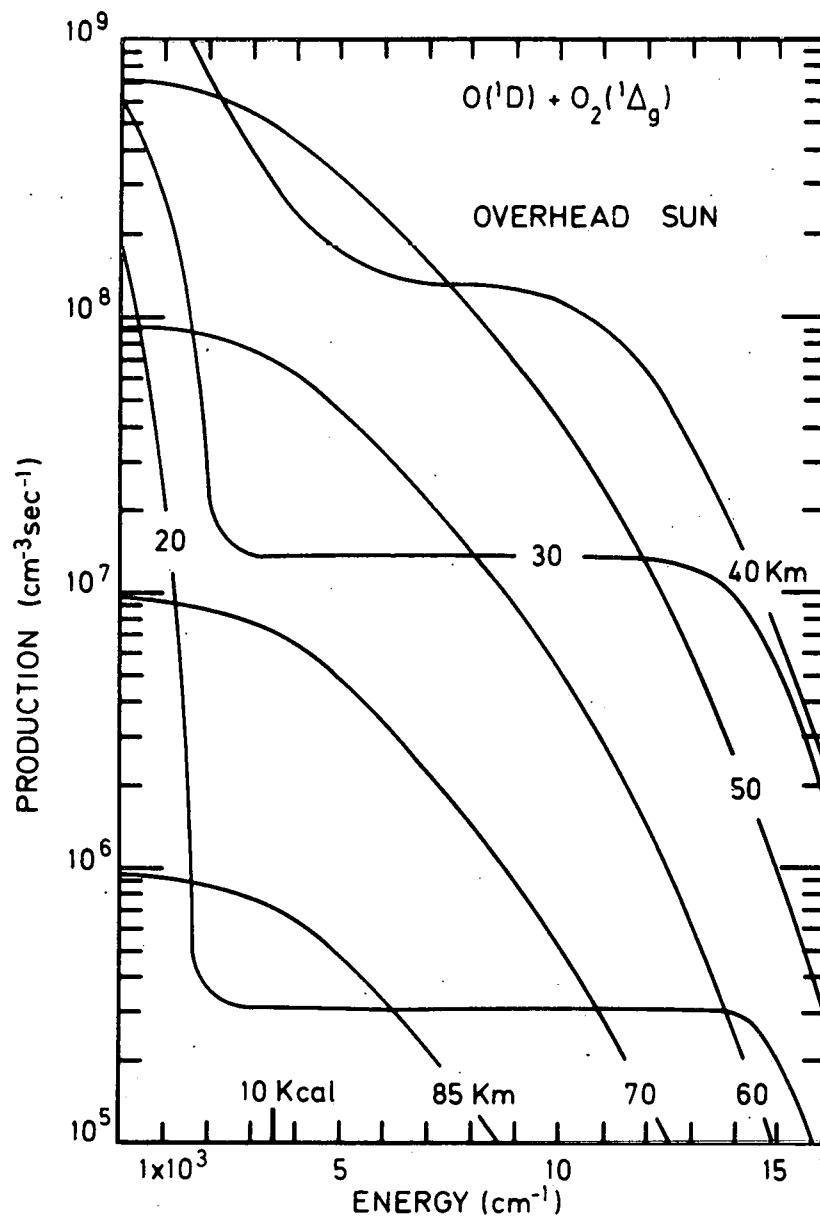


Fig. 6b.- Number ($\text{cm}^{-3} \text{sec}^{-1}$) of photodissociations of O_3 by $\lambda < 3100\text{\AA}$ leading to $O_2(^1\Delta_g)$ and $O(^1D)$ less than the energy indicated in cm^{-1} .

the exact efficiency is not sufficiently well known for $\lambda > 3100\text{\AA}$ (DeMore and Raper, 1966; Jones and Wayne, 1969; Wayne, 1971). Two values have been adopted here, $O(^1D)_{\max}$ and $O(^1D)_{\min}$, in order to compute the resulting production of nitric oxide molecules. They correspond to the production of $O(^1D)$ atoms at 3125\AA with 0.5 and 0.0 efficiency, respectively. The exact limit for the production of $O(^1D)$ atoms should be determined (see for example, Castellano and Schumacher, 1972) before obtaining exact values of the $O(^1D)$ production.

Considering all possible errors in the determination of the aeronomic rate coefficient it seems that errors of a factor of two cannot be avoided; as a result the production of nitric oxide molecules cannot yet be accurately determined. Furthermore, the exact vertical distribution of such a production is related to that of the N_2O concentration which, in turn, depends on transport conditions in the stratosphere.

If we consider the destruction of N_2O by photodissociation and by reaction with $O(^1D)$, the average total loss rate for day-and nighttime conditions at each height is given by

$$\frac{1}{2} n(N_2O) \left[J_{N_2O} + 2 \times 10^{-10} n(O(^1D)) \right] H_{N_2O} \quad (17)$$

This is compensated for, under steady state conditions, by a transport from the tropopause

$$\Phi_{N_2O} = n(N_2O) w_{N_2O} = n(N_2O) K \left[\frac{1}{H_{N_2O}} - \frac{1}{H_M} \right] \quad (18)$$

where w_{N_2O} is the vertical velocity of diffusion, K the eddy diffusion coefficient; H_{N_2O} and H_M are the N_2O and atmospheric scale heights, respectively. H_{N_2O} is defined by

$$-\frac{1}{H_{N_2O}} = \frac{1}{n(N_2O)} \frac{\partial n(N_2O)}{\partial z} + \frac{1}{T} \frac{\partial T}{\partial z} = \frac{1}{p(N_2O)} \frac{\partial p(N_2O)}{\partial z} \quad (19)$$

Fig. 7 shows the values of the eddy diffusion coefficient which are required in order to maintain a vertical distribution of N_2O in the stratosphere with scale heights $H_{N_2O} = 0.9 H_M$ and $H_{N_2O} = 1/2 H_M$. Impossibly high values of the eddy diffusion coefficient ($> 10^5 \text{ cm}^2 \text{ sec}^{-1}$) would be required in the upper stratosphere to maintain even a vertical distribution with $H_{N_2O} = 1/2 H_M$. In the lower stratosphere, values of the eddy

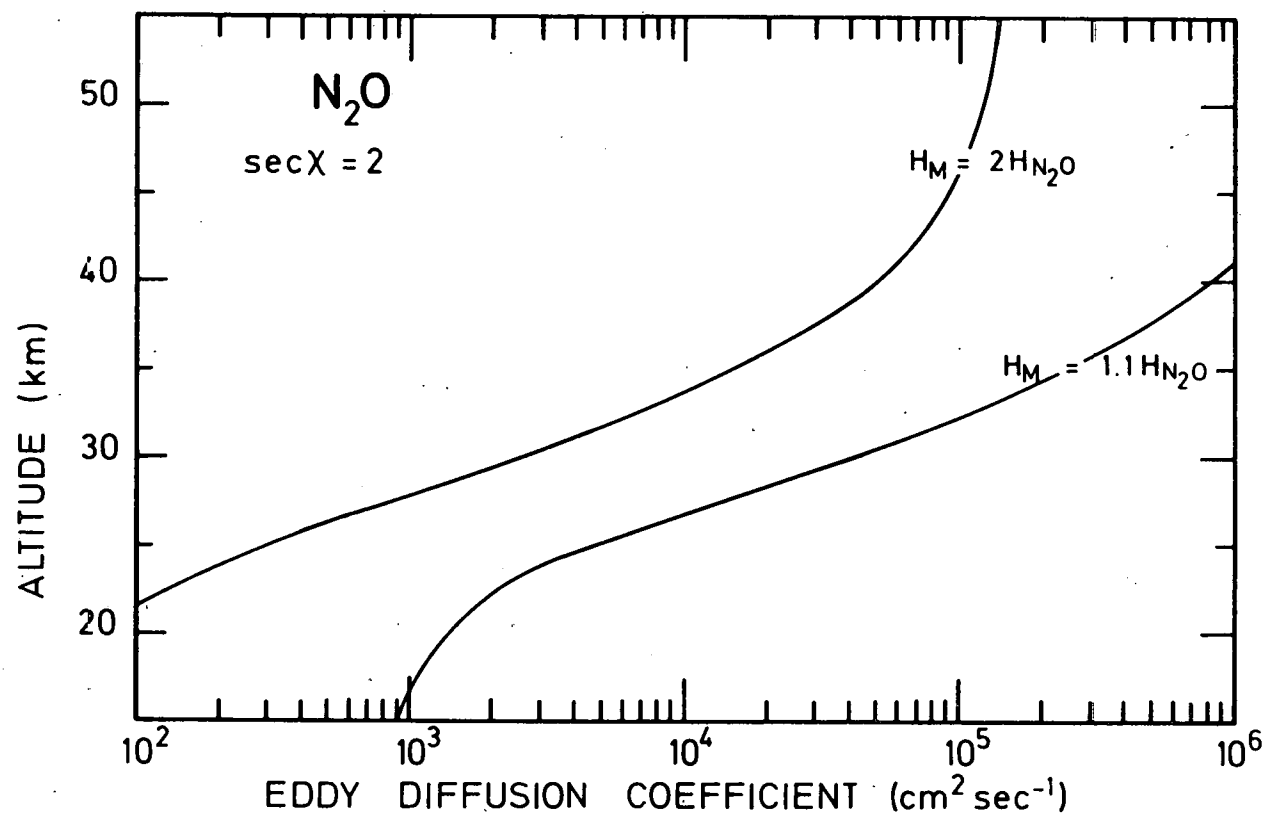


Fig. 7.- Eddy diffusion required to maintain a vertical distribution of N₂O with atmospheric scale height H_M corresponding to 1.1 H_{N₂O} and 2 H_{N₂O} for a solar zenith angle of 60°.

diffusion coefficients of the order of $2 \times 10^3 \text{ cm}^2 \text{ sec}^{-1}$ lead to a vertical distribution of N_2O following the atmospheric distribution. Thus, the transport equation for N_2O must be used in order to determine its vertical distribution according to various possible values of the eddy diffusion coefficient. It is written, from (17) and (18), for a steady state

$$\frac{\partial \Phi(\text{N}_2\text{O})}{\partial z} + \frac{1}{2} \left[n(\text{N}_2\text{O}) + 2 \times 10^{-10} n^*(\text{O}) \right] = 0 \quad (20)$$

Examples of various vertical distributions of nitrous oxide are given in Fig. 8: deduced from (20) with lower boundary conditions corresponding to a constant mixing ratio $n(\text{N}_2\text{O})/n(\text{M}) = 2.5 \times 10^{-7}$ at the tropopause, which is chosen here at 12 km, and a vanishing flux in the thermosphere above 150 km. When the eddy diffusion coefficient is less than $10^4 \text{ cm}^2 \text{ sec}^{-1}$ there is a rapid decrease in the slope of the N_2O mixing ratio with height as illustrated in Fig. 9. The mixing ratio decreases from 100 ppbv to 0.1 ppbv in a few kilometers.

It is clear that the vertical distribution of N_2O in the stratosphere depends strongly on the values of the eddy diffusion coefficients which are adopted (Nicolet and Vergison, 1971; McElroy and McDonnell, 1971). Furthermore, the vertical distribution also depends on the variation with height which is utilized for the eddy diffusion (see Fig. 10 for K_{\min} and K_{\max} used in Figs. 8 and 9). The stratospheric distribution of N_2O is very sensitive to the average conditions which are adopted; examples shown in Fig. 11 indicate that there is only a small difference between the curves giving N_2O concentrations for $\sec \chi = 1$ and $K = 10^3 \text{ cm}^2 \text{ sec}^{-1}$ and for $\sec \chi = 2$ and $K = 10^4 \text{ cm}^2 \text{ sec}^{-1}$. This must be kept in mind since it is not appropriate to assume the same average conditions with latitude and season, and it must be remembered that the average lifetime of an N_2O molecule in the stratosphere varies from a few days below the stratopause to many years in the neighbourhood of the tropopause.

Finally, considering limiting possibilities for the aeronomic conditions in the stratosphere (see Fig. 12) the flux of N_2O molecules from the troposphere into the stratosphere should be of the order of

$$F(\text{N}_2\text{O}) = (1 \pm 0.5) \times 10^9 \text{ cm}^{-2} \text{ sec}^{-1} \quad (21)$$

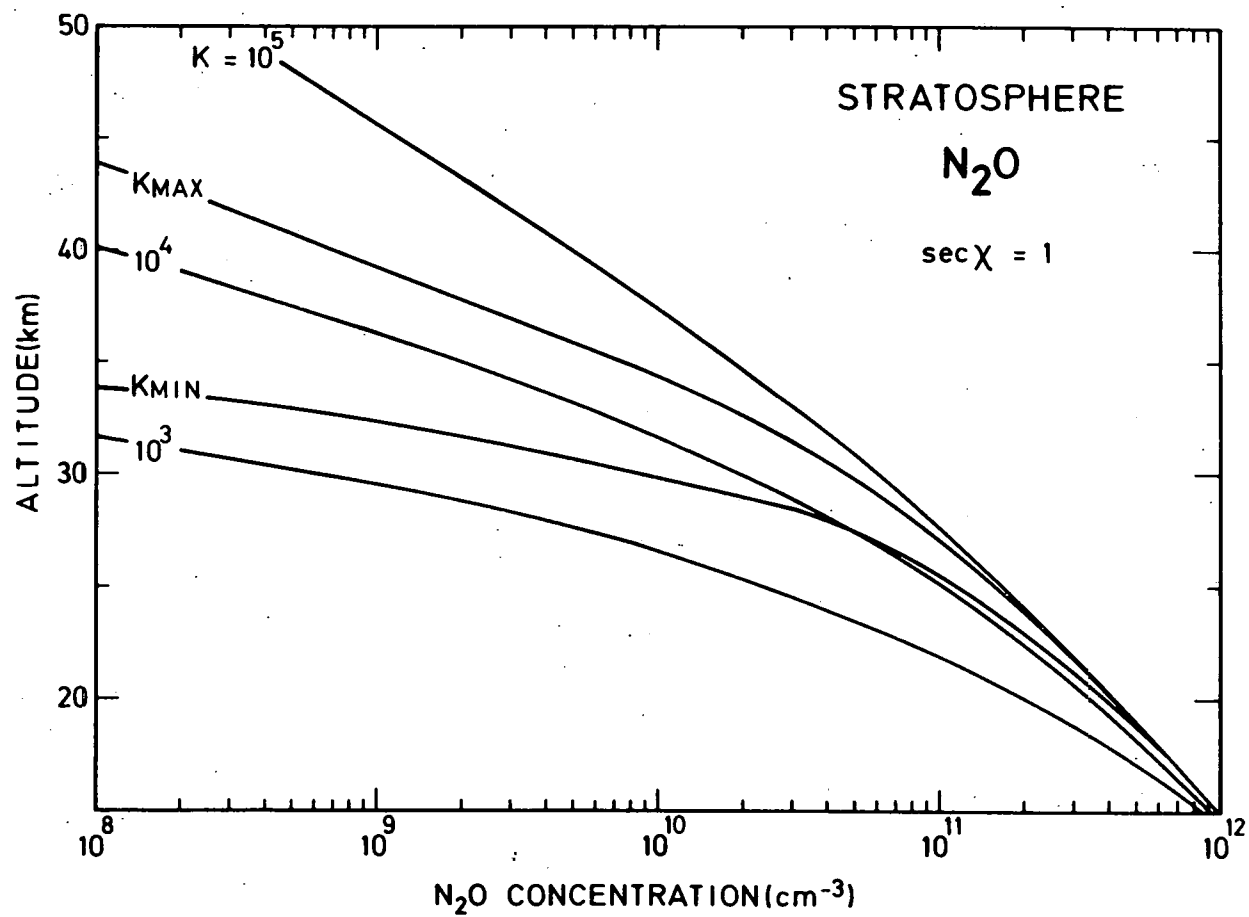


Fig. 8.- Vertical distributions of N₂O concentration in the stratosphere for various values of the eddy diffusion coefficient K(cm² sec⁻¹) and for overhead sun conditions.

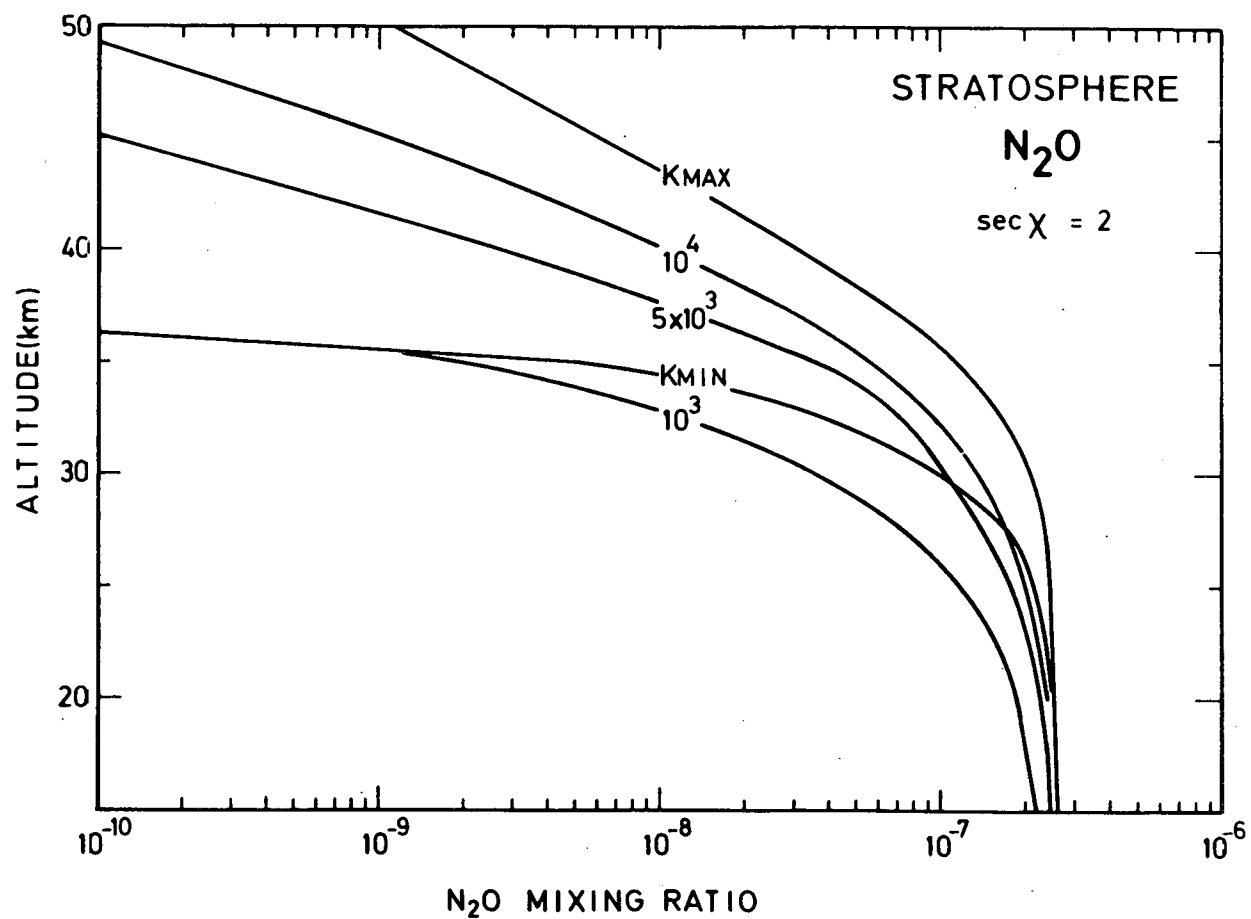


Fig. 9.- Variation of the nitrous oxide mixing ratio in the stratosphere for various values of the eddy diffusion coefficient $K(cm^2 sec^{-1})$ and for a solar zenith angle of 60° .

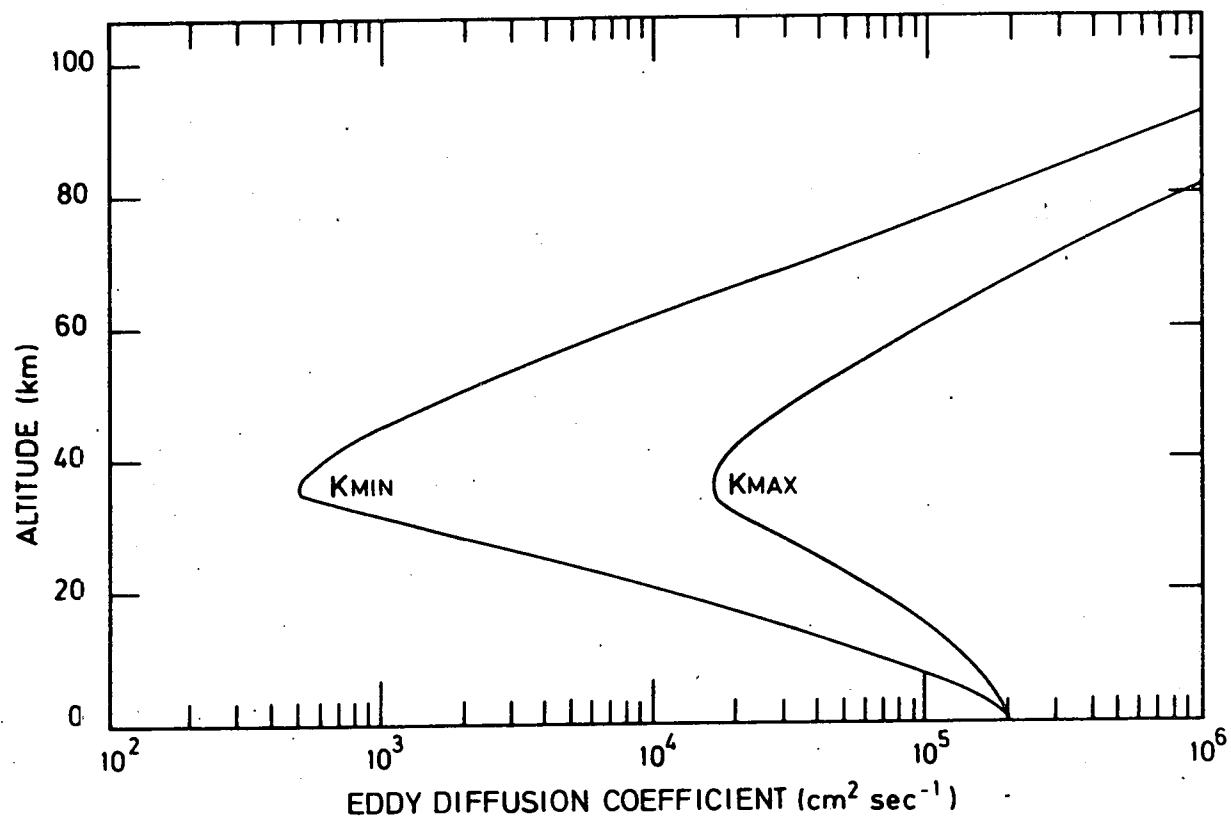


Fig. 10.- Minimum and maximum values of the eddy diffusion coefficient ($\text{cm}^2 \text{sec}^{-1}$) adopted in the stratosphere (and mesosphere) for calculation purposes.

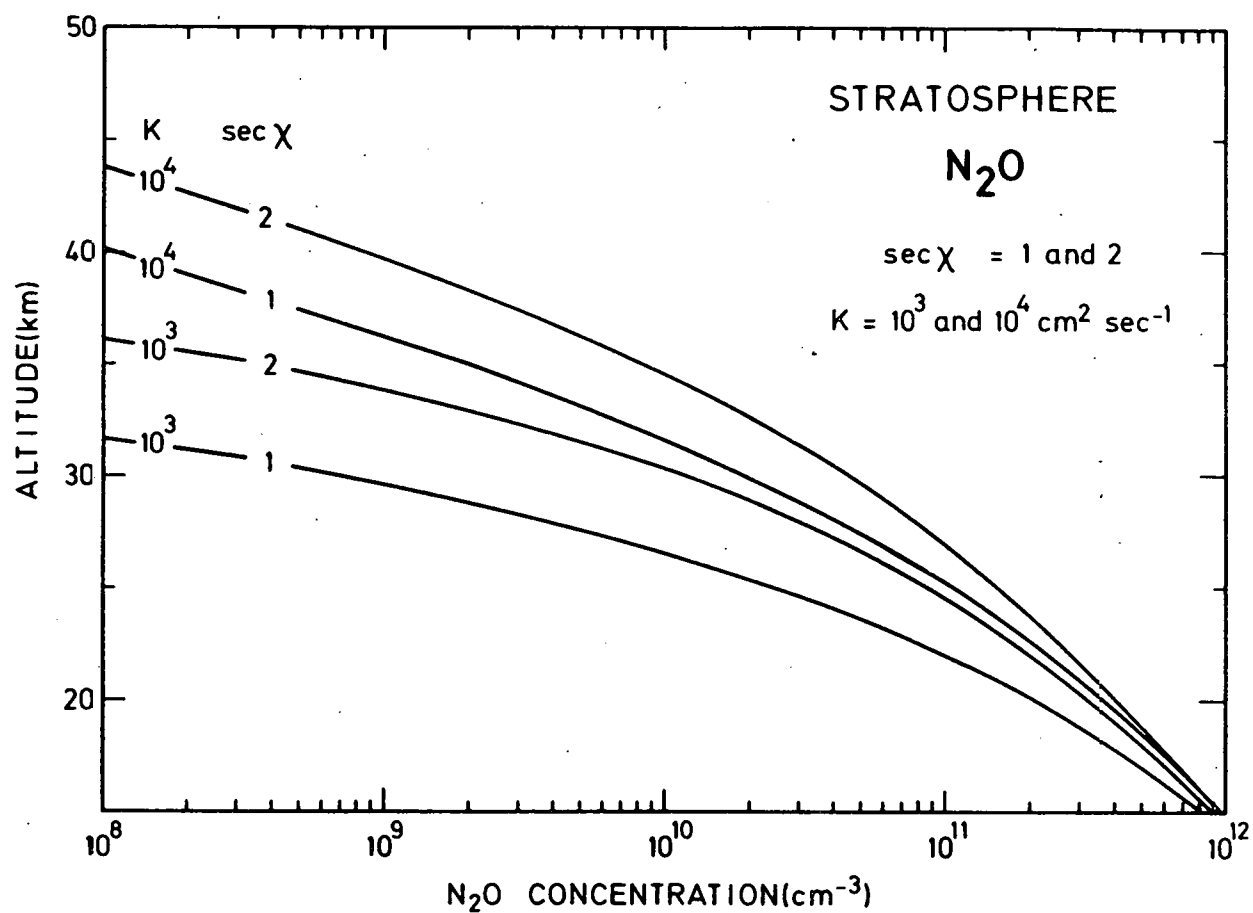


Fig. 11.- Comparison of average distribution of N₂O concentrations in the stratosphere for two extreme solar zenith angle conditions (sec χ = 1; 0° and sec χ = 2; 60°) and two eddy diffusion coefficients ($K = 10^3$ cm² sec⁻¹ and $K = 10^4$ cm² sec⁻¹).

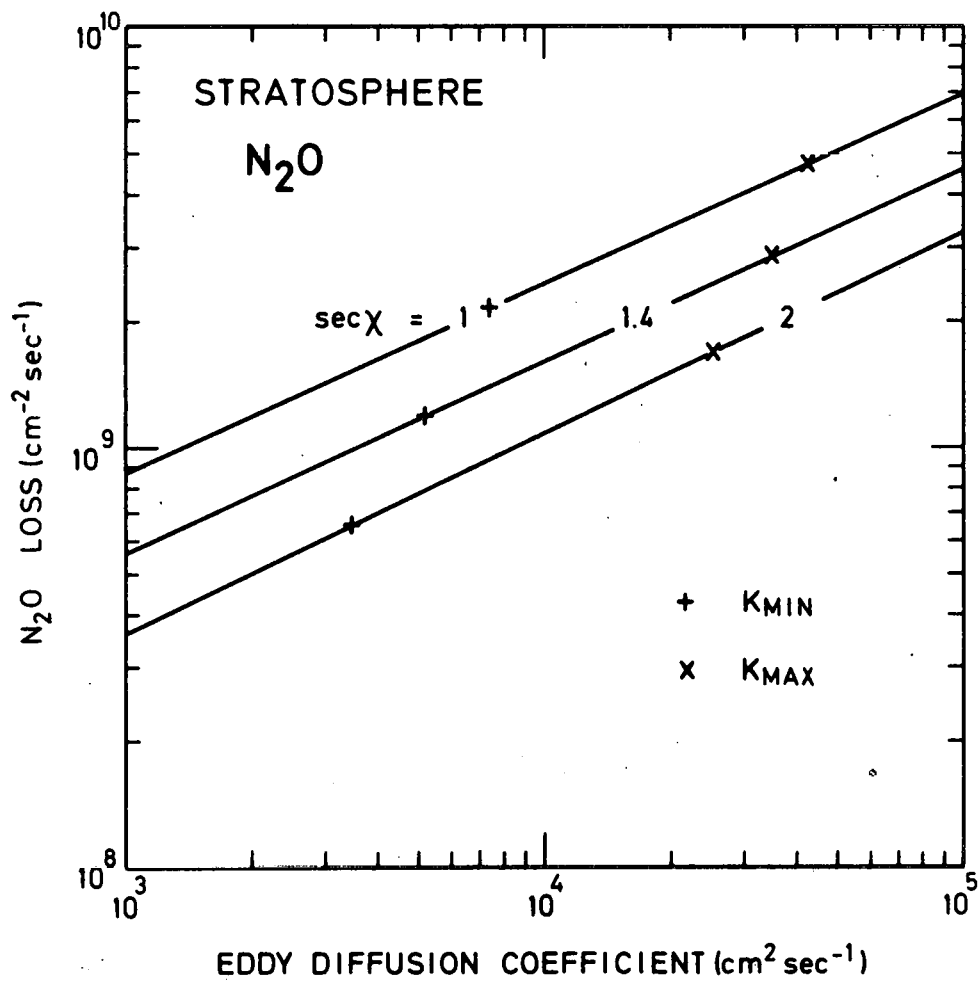


Fig. 12.- Total loss identical, under steady state conditions, to the total flux of N₂O molecules (cm⁻² sec⁻¹). Stratospheric conditions are given for solar conditions sec χ = 1, 1.4 and 2 and for eddy diffusion coefficients between 10³ cm² sec⁻¹ and 10⁵ cm² sec⁻¹. Tropopause at 12 km.

since average conditions should be represented by $1 < \sec \chi \leq 2$ and $10^3 < K < 10^4 \text{ cm}^2 \text{ sec}^{-1}$.

Considering the same stratospheric conditions for the production of nitric oxide by the reaction of $\text{O}(^1\text{D})$ with N_2O , the total natural production is of the order of (see Fig. 13)

$$P_n(\text{NO}) = (1.5 \pm 1) \times 10^8 \text{ cm}^2 \text{ sec}^{-1} \quad (22)$$

The vertical distribution of the production of nitric oxide depends not only on the vertical distribution of the ozone concentration in the stratosphere but also on the eddy diffusion coefficient and on its vertical distribution; particularly in the lower stratosphere. Furthermore, it is related to the exact vertical distribution of the concentrations of $\text{O}(^1\text{D})$ atoms in the lower stratosphere (see curves $\text{O}(^1\text{D})_{\text{Max}}$ and $\text{O}(^1\text{D})_{\text{Min}}$ in Fig. 14).

Another aspect of the problem of nitrogen oxides in the stratosphere is the transport of NO from the mesosphere and of NO_x from the troposphere. Such transports are not only related to the absolute value of the eddy diffusion coefficient but also depend on their relative scale heights. An upward transport of NO_x molecules requires a scale height H_{NO_x} which is less than the atmospheric scale height H_M , as can be seen from the conventional formula

$$F_{\text{NO}_x} = n(\text{NO}_x) \frac{K}{H_M} \left[\frac{H_M}{H_{\text{NO}_x}} - 1 \right] \quad (23)$$

As an example, H_{NO_x} should be $0.8 H_M$ and $0.3 H_M$ if the eddy diffusion coefficient values are 10^4 and $10^3 \text{ cm}^2 \text{ sec}^{-1}$, respectively, in order to obtain an upward flux of $5 \times 10^7 \text{ NO}$ molecules $\text{cm}^{-2} \text{ sec}^{-1}$ where the NO_x mixing ratio is chosen to be 3 ppbv.

Regarding a possible downward transport of nitric oxide from the mesosphere into the stratosphere, this requires a scale height H_{NO} greater than the atmospheric scale height. For example, a scale height $H_{\text{NO}} = 2 H_M$ (see formula 23) requires, with an eddy diffusion coefficient of the order of $10^5 \text{ cm}^2 \text{ sec}^{-1}$, NO concentrations of not less than $8 \times 10^8 \text{ molecules cm}^{-3}$ (40 ppbv) in order to obtain a downward flux of $5 \times 10^7 \text{ cm}^2 \text{ sec}^{-1}$. This corresponds to the minimum production rate of NO molecules in the stratosphere as given by expression (22).

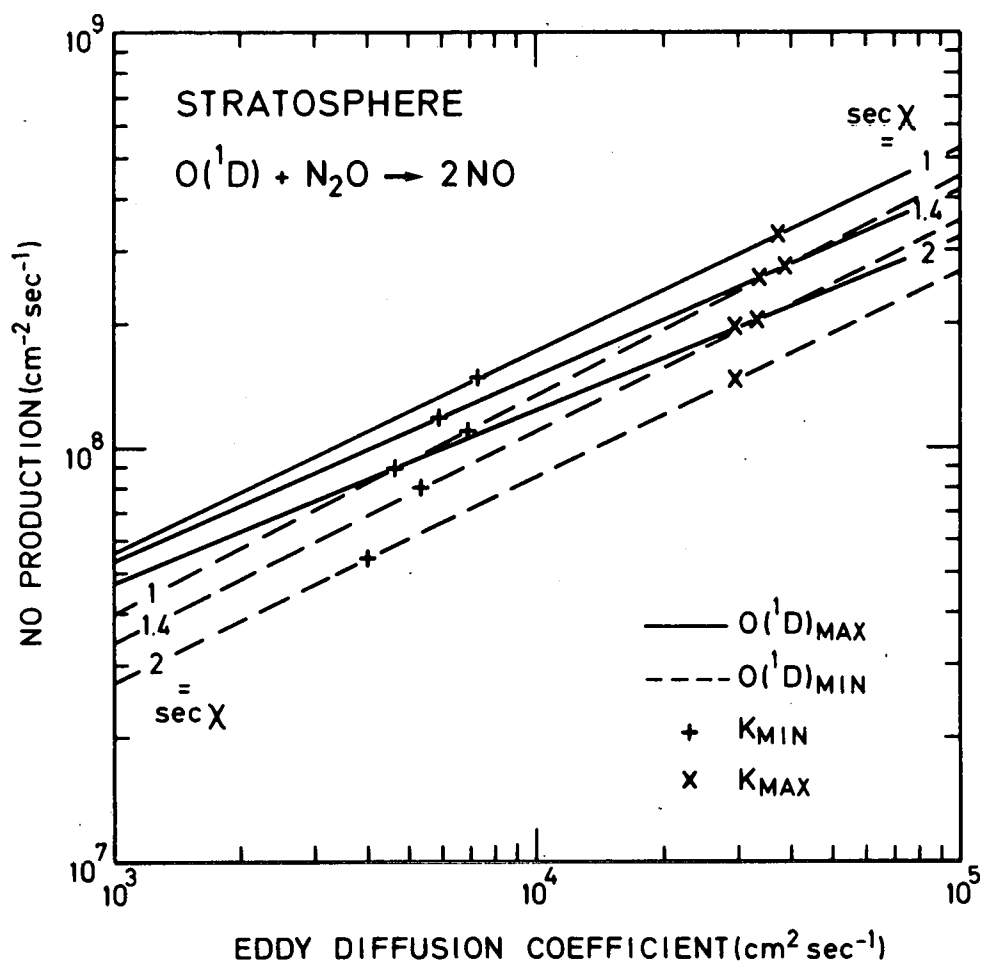


Fig. 13.- Total production of nitric oxide molecules ($\text{cm}^{-2} \text{sec}^{-1}$) due to the reaction $O(^1D) + N_2O \rightarrow 2NO$. Stratospheric conditions for sec $\chi = 1, 1.4$ and 2 and $10^3 < K < 10^4 \text{ cm}^2 \text{sec}^{-1}$. Tropopause at 12 km and two values assumed for $O(^1D)$.

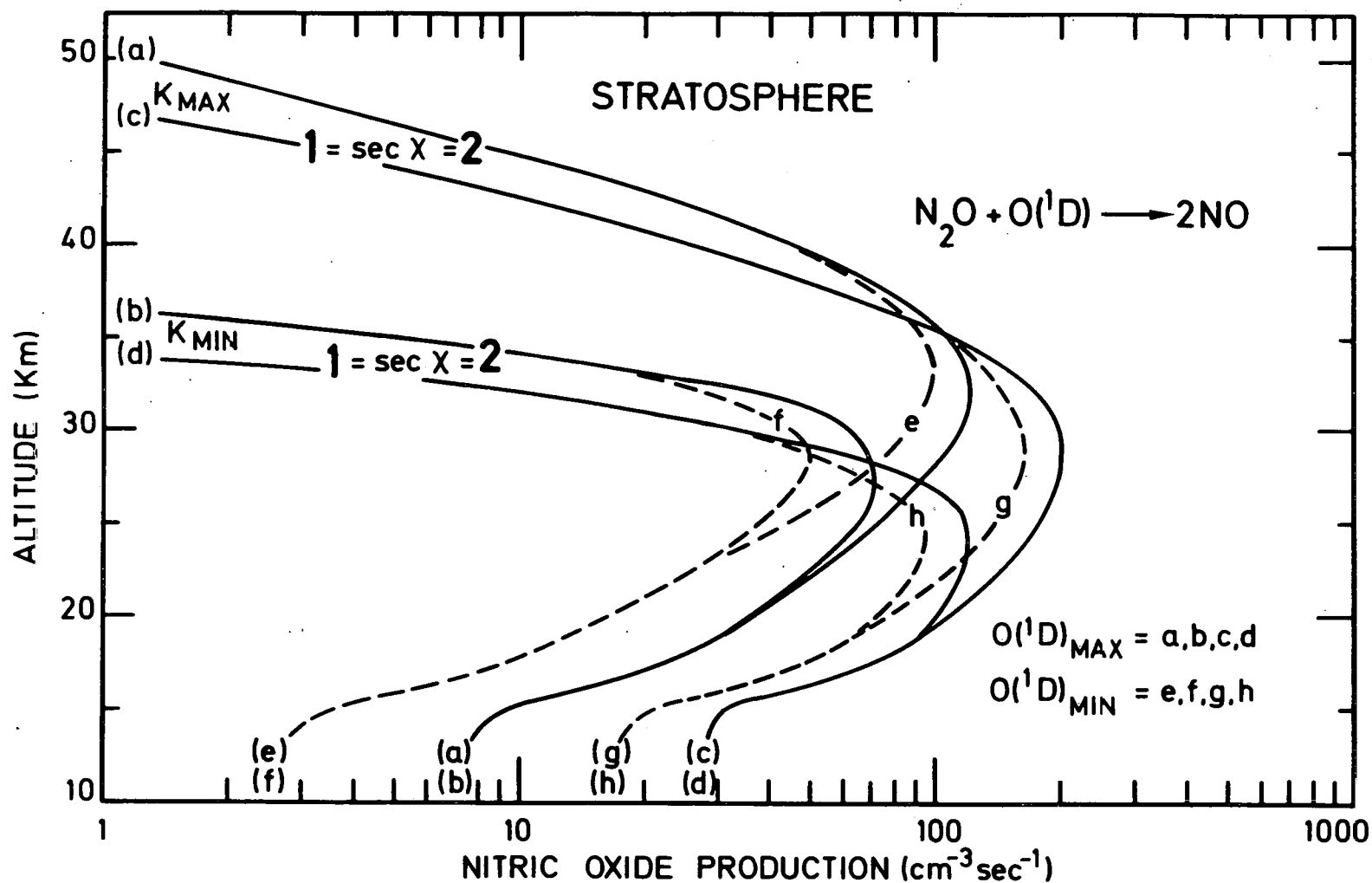


Fig. 14.- Vertical distribution of NO production ($\text{cm}^{-3}\text{sec}^{-1}$) for various stratospheric conditions sec χ = 1 and 2; $K = 10^3$, $10^4\text{ cm}^2\text{sec}^{-1}$; $\text{O}(^1\text{D})_{\text{MAX}}$ and $\text{O}(^1\text{D})_{\text{MIN}}$.

An additional production of NO, by an increase of N_2O formed by chemical reaction (1) between N_2 and O_3 , does not appear to be important if its reaction rate coefficient, of the order of $10^{-28} \text{ cm}^3 \text{ sec}^{-1}$ at 300° K, has an activation energy of the order of 20 kcal. It can be seen that this production rate is negligible compared with the destruction rate of N_2O by photodissociation in the stratosphere. The rate coefficient $10^{-12} e^{-11000/T}$ would be of the order of 10^{-34} at the tropopause and about 2×10^{-29} at the stratopause. At this level, however, an effect can occur when a low value, such as $10^3 \text{ cm}^2 \text{ sec}^{-1}$ is adopted for the eddy diffusion coefficient. But such an effect is not important compared with the entire production of NO in the stratosphere. If a reaction rate coefficient of the order of $10^{-28} \text{ cm}^3 \text{ sec}^{-1}$ were adopted for stratospheric temperatures of the order of 200° K, the result would be an important increase of N_2O and of NO production. But such a high rate coefficient would require experimental verification at such low temperatures.

Finally, if we consider that the emission of nitric oxide is of the order of 10 ± 2.5 grams per kilogram of fuel consumed by a supersonic jet flying in the stratosphere (instead of 42 gm/kgm indicated in SCEP, 1970) we obtain, for a conventional 500 SST aircraft (334 equipped with four engines and 166 with two engines) flying for almost 7 hours a day (SCEP, 1970; SMIC, 1971), a yield of nitric oxide of the order of $6.7 \times 10^{11} \text{ gm/year}$ corresponding to an average of $8.5 \times 10^7 \text{ NO molecules cm}^{-2} \text{ sec}^{-1}$. Such a value is of the same order of magnitude as the natural production of nitric oxide from stratospheric nitrous oxide given by expression (22).

Another process which can produce nitric oxide in the stratosphere is the reaction of nitrogen atoms with molecular oxygen. This leads, in less than 10 seconds in the lower stratosphere, to nitric oxide molecules. The production of nitrogen atoms in the stratosphere is related to the normal ionization by cosmic rays and to the exceptional ionization by charged particles. At the altitude of 25 km, the number of ion pairs produced (STP conditions with mean solar activity at geomagnetic latitude 50°) is of the order of $275 \text{ cm}^{-3} \text{ sec}^{-1}$. This corresponds to an ionization coefficient of about $10^{-17} \text{ sec}^{-1}$ and leads to a production of not less than $10 \text{ ions cm}^{-3} \text{ sec}^{-1}$ in the lower stratosphere. If we consider that the ionization coefficient may vary (from Neber's data, 1969, private communication) from $2 \times 10^{-18} \text{ sec}^{-1}$ (equator, all conditions) to $2 \times 10^{-17} \text{ sec}^{-1}$ (high latitudes, maximum solar

activity), the total ionization in the lower stratosphere may correspond to an ion production varying from 5×10^6 to 5×10^7 ions $\text{cm}^{-2} \text{sec}^{-1}$. It is not known which part of this ion production may correspond to a dissociative ionization or perhaps to a direct dissociation of N_2 . If this were not a negligible percentage, the action of cosmic rays in the production of NO molecules could not be neglected at high latitudes.

Thus, more measurements are needed before determining with sufficient accuracy the stratospheric distribution of N_2O and the importance of the secondary sources of nitric oxide in the stratosphere in comparison with the production by the reaction of electronically excited oxygen atom $\text{O}(^1\text{D})$ with nitrous oxide.

REFERENCES

- ACKERMAN, M., Ultraviolet solar radiation related to mesospheric processes, in *Mesospheric Models and Related Experiments*, Ed. Fiocco, p. 149, Reidel Cy, Dordrecht, 1971.
- ADEL, A., Note on the atmospheric oxides of nitrogen, *Astrophys. J.*, **90**, 627, 1939.
- ADEL, A., Rotational structure of the nitrous oxide (NNO) band ν_1 at 7.78μ , *Astrophys. J.*, **93**, 589, 1941.
- ADEL, A., A possible source of atmospheric N_2O , *Science*, **103**, 280, 1946.
- ADEL, A., Atmospheric nitrous oxide and the nitrogen cycle, *Science*, **113**, 624, 1951.
- BATES, D.R. and HAYS, P.B., Atmospheric nitrous oxide, *Planet. Space Sc.*, **15**, 189, 1967.
- BATES, D.R. and WITHERSPOON, A.E., The photo-chemistry of some minor constituents of the earth's atmosphere (CO_2 , CO, CH_4 , N_2O), *Month. Notices Roy. Astr. Soc.*, **112**, 101, 1952.
- BIRKELAND, J.W. and SHAW, J.H., Abundance of nitrous oxide in ground-level air, *J. Opt. Soc. Amer.*, **49**, 637, 1959.
- BOWMAN, R.L. and SHAW, J.H., The abundance of nitrous oxide, methane and carbon monoxide in ground-level air, *Applied Optics*, **2**, 176, 1963.
- CASTELLION, G.A. and NOYES, W.A., Photochemical studies L II, The nitrous oxide-ethane system, *J. Amer. Chem. Soc.*, **79**, 290, 1957.
- CASTELLANO, E. and SCHUMACKER, H.J., The kinetics and the mechanism of the photochemical decomposition of ozone with light of 3340\AA wavelength, *Chem. Phys. Lett.*, **13**, 625, 1972.
- CLYNE, M.A.A. and THRUSH, B.A., Mechanism of chemiluminescent combination reactions involving oxygen atoms, *Proc. Roy. Soc.*, **269A**, 404, 1962.
- CRUTZEN, P.J., The influence of nitrogen oxides on the atmospheric ozone content, *Quartely J.R. Met. Soc.*, **96**, 320, 1970.
- DEMORE, W.B., Reactions of $O(^1D)$ with hydrocarbons in liquid argon, *J. Phys. Chem.*, **73**, 391, 1969.
- DEMORE, W.B., $O(^1D)$ quenching efficiency of O_2 relative to other gases, *J. Chem. Phys.*, **52**, 4309, 1970.
- DEMORE, W.D. and RAPER, O.F., Primary processes in the ozone photolysis, *J. Chem. Phys.*, **44**, 1780, 1966.
- DIBELER, V.H., N_2 bond dissociation energy by photon impact, *J. Chem. Phys.*, **47**, 2191, 1967.

- DONOVAN, R.J., HUSAIN, D. and KIRSCH, L.J., Relative rate data for the quenching of $O(2^1D_2)$ using the OH radical as a spectroscopic marker, *Chem. Phys. Letters*, **6**, 488, 1970.
- FISHBURNE, E.S. and EDSE, R., Reaction between atomic oxygen and nitrous oxide, *J. Chem. Phys.*, **44**, 515, 1966.
- GAUTHIER, M. and SNELLING, D.R., Mechanism of singlet molecular oxygen formation from photolysis of ozone at 2537\AA , *J. Chem. Phys.*, **54**, 4317, 1971.
- GILPIN, R., SCHIFF, H.I. and WELGE, K.H., Photodissociation of O_3 in the Hartley band. Reactions of $O(^1D)$ and $O_2(^1\Sigma_g^+)$ with O_3 and O_2^* , *J. Chem. Phys.*, **55**, 2087, 1971.
- GOLDBERG, L. and MULLER, E.A., The vertical distribution of nitrous oxide and methane in the earth's atmosphere, *J. Opt. Soc. Amer.*, **43**, 1033, 1953.
- GOLDMAN, C.S., GREENBERG, R.I. and HEICKLEN, J., The reactions of $O(^1D)$ with ozone and nitrous oxide, *Intern. J. Chem. Kinet.*, **3**, 501, 1971.
- GOLDMAN, A., MURCRAY, D.G., MURCRAY, F.H., WILLIAMS, W.J., KYLE, T.G. and BROOKS, J.N., Abundance of N_2O in the atmosphere between 4.5 and 13.5 km, *J. Opt. Soc. Amer.*, **60**, 1466, 1970.
- GOODY, R.M., *The physics of the stratosphere*, Cambridge Un. Press, 1954.
- GOODY, R.M., Time variations in atmospheric N_2O in Eastern Massachusetts, *Astr. J.*, **17**, 1319, 1969.
- GOODY, R.M. and WALSHAW, C.D., The origin of atmospheric nitrous oxide, *Quart. J. Roy. Meteor. Soc.*, **79**, 496, 1953.
- GREENBERG, R.I. and HEICKLEN, J., Reaction of $O(^1D)$ with N_2O , *Intern. J. Chem. Kinet.*, **2**, 185, 1970.
- HESSTVEDT, E., and JANSSON, U.B., On the effect of vertical eddy transport on the distribution of neutral nitrogen components in the D-region, *Aeronomy Report, Univ. Illinois*, nr 32, 190, 1969.
- HOLLIDAY, M.G. and REUBEN, B.G., Temperature dependence of the absorption of nitrous oxide in the quartz ultraviolet, *Trans. Faraday Soc.*, **64**, 1735, 1968.
- JONES, I.T.N. and WAYNE, R.P., The photolysis of ozone by 254 nm, 313 nm and 334 nm radiation, *J. Chem. Phys.*, **51**, 3617, 1969.
- JUNGE, C., and HAHN, J., N_2O measurements in the North Atlantic, *J. Geophys. Res.*, **76**, 8143, 1971.
- LA HUE, M.D., PATE, J.B., LODGE, J.P., Atmospheric nitrous oxide concentrations in the humid tropics, *J. Geophys. Res.*, **75**, 2922, 1970.

- LISSI, E. and HEICKLEN, J., The photolysis of ozone, *Ionosphere Res. Lab., Penn. State Sci. Report*, nr 387, 1972.
- LOWENSTEIN, M., Relative quenching rates of $O(^1D)$ by CO_2 , N_2 and O_2 , *J. Chem. Phys.*, **54**, 2282, 1971.
- McELROY, M.B. and McCONNELL, J.C., Nitrous oxide : A natural source of stratospheric NO, *J. Atmos. Sci.*, **28**, 1095, 1971.
- McDANIEL, E.W., Collision phenomena in ionized gases, J. Wiley, New York, 1964.
- NICOLET, M., Ozone and hydrogen reactions, *Annales Géophys.*, **26**, 531, 1970.
- NICOLET, M., Aeronomic reactions of hydrogen and ozone, *Aeronomica Acta A*, nr 79, 1970 and pp. 1-51 in *Mesospheric Models and Related Experiments*, Reidel Cy, Dordrecht, 1971.
- NICOLET, M. and VERGISON, E., L'oxyde azoteux dans la stratosphère, *Aeronomica Acta A*, nr 91, 1971.
- NOXON, J.F., Optical emissions from $O(^1D)$ and $O_2(b^1\Sigma_g)$ in the ultraviolet photolysis of O_2 and CO_2 , *J. Chem. Phys.*, **52**, 1852, 1970.
- OKABE, H., Excited species and their contribution to $NO(\beta, \gamma)$ fluorescence in the photodissociation of N_2O , *J. Chem. Phys.*, **47**, 101, 1965.
- PARASKEVOPOULOS, G. and CVETANOVIC, R.J., Competitive reactions of the excited oxygen atoms, $O(^1D)$, *J. Amer. Chem. Soc.*, **91**, 7572, 1969.
- PARASKEVOPOULOS, G. and CVETANOVIC, R.J., Relative rate of reaction of $O(^1D)$ with H_2O , *Chem. Phys. Letters*, **9**, 603, 1971.
- PARASKEVOPOULOS, G., PRESTON, K.F. and CVETANOVIC, R.J., Relative rate of deactivation of $O(^1D_2)$ by molecular oxygen, *J. Chem. Phys.*, **54**, 3907, 1971.
- PRESTON, K.F. and BARR, R.F., Primary processes in the photolysis of nitrous oxide, *J. Chem. Phys.*, **54**, 3347, 1971.
- RANK, D.H., SLOMBA, A.F., GARDNER, E.F. and WIGGINS, T.A., Abundance of N_2O in the atmosphere, *J. Opt. Soc. Amer.*, **52**, 858, 1962.
- REUBEN, B.G. and LINNETT, J.W., Thermal decomposition of nitrous oxide, *Trans. Faraday Soc.*, **55**, 1543, 1959.
- SCEP, Report of the Study of Critical Environmental Problems, Man's Impact on the Global Environment, The MIT Press, Cambridge Mass., 1970.
- SCHUTZ, K., JUNGE, C., BECK, R. and ALBRECHT, B., Studies of atmospheric N_2O , *J. Geophys. Res.*, **75**, 2230, 1970.

- SCOTT, P.M. and CVETANOVIC, R.J., Relative rate constant for reactions of $O(^1D)$ atoms generated by flash photolysis of ozone, *J. Chem. Phys.*, **54**, 1440, 1971.
- SCOTT, P.M., PRESTON, K.F., ANDERSEN, R.J. and QUICK, L.M., The reaction of the electronically excited oxygen atom $O(^1D_2)$ with nitrous oxide, *Canadian J. Chem.*, **49**, 1808, 1971.
- SEELEY, J.S. and HOUGHTON, J.T., Spectroscopic observations of the vertical distribution of some minor constituents of the atmosphere, *Infrared Phys.*, **1**, 116, 1961.
- SHIMAZAKI, T. and LAIRD, A.R., A model calculation of the diurnal variation in minor neutral constituents in the mesosphere and lower thermosphere including transport effects, *J. Geophys. Res.*, **75**, 3221, 1970.
- SIMONAITIS, R., GREENBERG, R.I. and HEICKLEN, J., The photolysis of N_2O at 2139 \AA and 1849 \AA , *Ionosphere Res. Lab. Penn. State Univ., Sci. Report*, nr 384, 1972.
- SIMONAITIS, R., LISSI, E. and HEICKLEN, J., Production of N_2O from the reaction of $O(^1D)$ with N_2 , in press, 1972.
- SMIC, Report of the Study of Man's Impact on Climate, Inadvertent Climate Modification, The MIT press, Cambridge, Mass., 1971.
- SNELLING, D.R. and BAIR, E.J., Deactivation of $O(^1D)$ by molecular oxygen, *J. Chem. Phys.*, **48**, 5737, 1968.
- SPONER, H. and BONNER, L.G., Note on the continuous absorptions of N_2O , *J. Chem. Phys.*, **8**, 33, 1940.
- STEARN, A.E. and EYRING, H., Nonadiabatic reactions. The decomposition of N_2O , *J. Chem. Phys.*, **3**, 778, 1935.
- STUHL, F., and NIKI, H., Measurements of rate constants for termolecular reactions of $O(^3P)$ with NO , O_3 , CO , N_2 and CO_2 using a pulsed vacuum-uv photolysis-chemiluminescent method, *J. Chem. Phys.*, **55**, 3943, 1971.
- THOMPSON, B.A., HARTECK, P. and REEVES, R.R., Ultraviolet absorption coefficients of CO_2 , CO , O_2 , H_2O , N_2O , NH_3 , NO , SO_2 , and CH_4 between 1850 and 4000 \AA , *J. Geophys. Res.*, **68**, 6431, 1963.
- WAYNE, R.P., The photochemistry of ozone and singlet molecular oxygen in the atmosphere, pp. 240-252 in *Mesospheric Models and Related Experiments*, Reidel Cy, Dordrecht 1971.
- YAMAZAKI, H., On the deexcitation of the singlet excited oxygen atoms, *Canadian J. Chem.*, **48**, 3269, 1970.

- YOUNG, R.A., BLACK, G. and SLANGER, T.G., Reaction and deactivation of $O(^1D)$, *J. Chem. Phys.*, **49**, 4758, 1968.
- ZELIKOFF, M. and ASCHELBRAND, L.M., Vacuum ultraviolet photochemistry, Part II Nitrous oxide at 1849\AA , *J. Chem. Phys.*, **22**, 1685, 1954.
- ZELIKOFF, M., WATANABE, K. and YNN, E.C.Y., Absorption coefficients of gases in the vacuum ultraviolet. Part II. Nitrous oxide, *J. Chem. Phys.*, **21**, 1643, 1953.